

Hydrolysis and Condensation Mechanisms of a Silane Coupling Agent Studied by ^{13}C and ^{29}Si NMR

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Synopsis

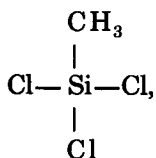
The mechanisms of hydrolysis and condensation of a silane coupling agent, γ -methacryloxypropyltrimethoxysilane (γ -MPTS) were investigated by the use of both ^{13}C and ^{29}Si nuclear magnetic resonance (NMR) spectroscopies. The NMR peaks of the hydrolyzed monomer and condensed polymer were assigned readily. The rate of hydrolysis and condensation of γ -MPTS was dependent on water content. On the basis of the time-dependent behavior of these peaks, the mechanisms of hydrolysis and condensation were clear.

INTRODUCTION

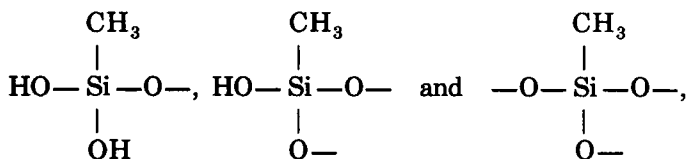
It is well known that silica glass is treated with a silane coupling agent in order to reinforce the bonding between silica and matrix resin.

Schrader et al.¹ classified the adsorbed silane layers on the silica surface into three regions; the first layer consists of covalent bond layer to silica surface, the second layer consists of hydrogen bond layer, and the third layer consists of silane molecules which were condensed by cohesive force. Ishida et al.^{2,3} studied the physisorbed silane layer of γ -methacryloxypropyltrimethoxysilane (γ -MPTS), removed it from the clay surface using the fourier transform infrared (FT-IR) method, and assigned the physisorbed silane layer to a caged polycyclic or random connected beaded-chain structure, from the presence of Si—O—Si bands 1106, 1080, and 1064 cm^{-1} . The structure of γ -MPTS deposited on the surface of various particulate mineral fillers depends strongly on the acid/base character of the substrate, such as clay and zinc oxide. Miller et al.⁴ studied the substrate pH effect on the molecular structure of deposited γ -MPTS by adjusting the solution pH in detail using FT-IR and gel permeation chromatography (GPC) methods. The hydrolyzates obtained from the solution were polymethacryloxypropylsilsequioxanes, whose configuration and molecular-weight distribution were dependent on the pH solutions. In acidic environments (below pH 4) the polycondensation mechanisms appeared to proceed in a selective manner from polycyclic blocks, which resemble a beaded chain to condensation between blocks. Under more neutral and basic condensations (at or above pH 4) the polycondensation mechanism resulted in polymethacryloxypropylsilsequioxanes, with a more equilibrated double chain ladder configuration. However, it is well known that the bands between 1,200 and 1,000 cm^{-1} are also assigned to the Si—O—Si bands of the open chain, such as $-(\text{Si}-\text{O})_n-$, not to the ladder and cyclic chain.⁵

Therefore, it is difficult to assign this particular structure to only the band in the IR spectrum. Sindorf et al.^{6,7} studied the condensation of the silane molecules,



reaction with silica gel by the use of the CP/MAS ²⁹Si NMR method. The appearance of the ²⁹Si peaks, assigned to



makes it possible to clarify the aspect of the condensation of the silane monomer adsorbed on to the silica surface. Thus, the NMR method is useful for analysis of the hydrolysis and condensation of the silane molecules. This is due to the good resolution and ease of assignment of the ²⁹Si NMR peaks of silane molecules in comparison with the IR spectrum method. In addition, several kinds of hydrolyzed species, and the change of the relative fraction of such species, are directly observable in the silane solution.

In our previous papers,⁸⁻¹² the aspects of the silane coupling agent adsorbed on the silica surface were investigated with spin-labeled ESR method. In particular, ESR signals of the spin-labeled agents adsorbed on to the colloidal silica surface were composed of two components; a slow mobile component attributable to the agents adsorbed directly on the Si—OH groups of the silica surface and a rapid mobile one attributable to the agents interacted with such adsorbed silane molecules. In order to assign the molecular species, and to clarify by what mechanisms the silane molecule was adsorbed onto the colloidal silica surface, it is necessary to obtain detailed information on a molecular level concerning the hydrolysis and condensation of the silane coupling agent.

In this study, both ¹³C and ²⁹Si NMR spectroscopies are applied to clarify the hydrolysis and condensation mechanisms of the γ -MPTS in EtOH—H₂O solution.

EXPERIMENTAL

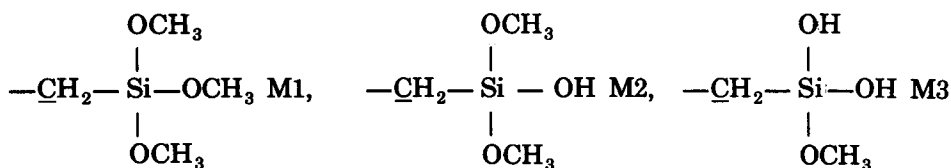
A silane coupling agent, γ -MPTS which was purchased from Japan UCC Co., was dissolved in a EtOH—H₂O solution at 20 °C. The water was distilled (pH = 5.7). Then, the ¹³C and ²⁹Si NMR spectra were measured periodically at 23 °C. The composition of the EtOH—H₂O solution was changed; 90 : 10, 80 : 20, 70 : 30, 60 : 40 in vol%. The NMR spectra were obtained with a JEOL FX-90Q spectrometer at 23 °C, operating at 22.49 MHz (¹³C) and 17.75 MHz (²⁹Si). The scans and repetition time were 200–400 and 3.8 s, respectively, for the ¹³C NMR measurement and were 60–800 and 51 s, respectively, for the ²⁹Si NMR measurement.

RESULTS AND DISCUSSION

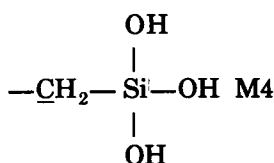
Assignment of the ^{13}C NMR peaks of γ -MPTS

The ^{13}C NMR spectrum of γ -MPTS is shown in Figure 1. The silane coupling agent was hydrolyzed for two days in 70 vol% EtOH-H₂O solution. The peak assigned to each carbon atom was readily performed as shown in Figure 1. Observation of the methyl peak of methanol indicates the hydrolysis of the methoxy group of γ -MPTS. In addition, the α -CH₂ carbon peak of γ -MPTS split into several peaks, reflecting the presence of several kinds of the hydrolysis species. The corresponding splitting was also observed at the β -CH₂ and γ -CH₂ carbon peaks. The width of the α -CH₂ peak splitting was largest among these peaks and thus, it is easy to follow the hydrolysis process of γ -MPTS from the spectral change in the α -CH₂ peaks. Thus, detailed examination of the ^{13}C NMR spectrum of γ -MPTS was limited for the α -CH₂ peak.

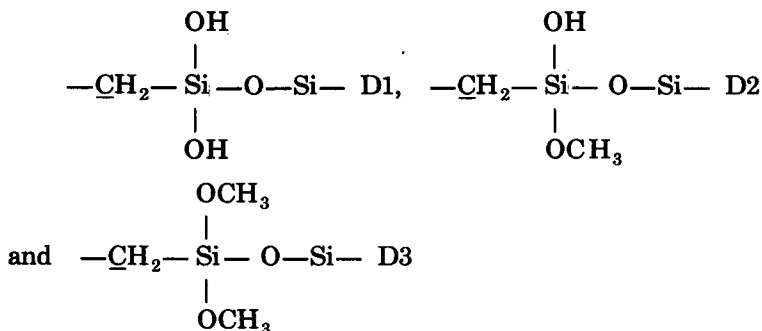
The α -CH₂ resonance region is expanded in Figure 2. In the first day spectrum, the α -CH₂ peaks are classified into four regions. The ^{13}C NMR spin-lattice relaxation times, T_1 , are included in the second day spectrum, and tend to decrease for the peaks resonating at lower fields. The decrease in mobility implies the formation of intermolecular hydrogen bonding among the hydrolysis products. Thus, the peaks observed in the 1st day spectrum were assigned to



and



to lower fields. In addition, the D1, D2, and D3 peaks have shorter T_1 values than the M4, M3, and M2 peaks, respectively, indicating that these peaks are attributable to the dimerized species. Thus, D1, D2, and D3 peaks were assigned to



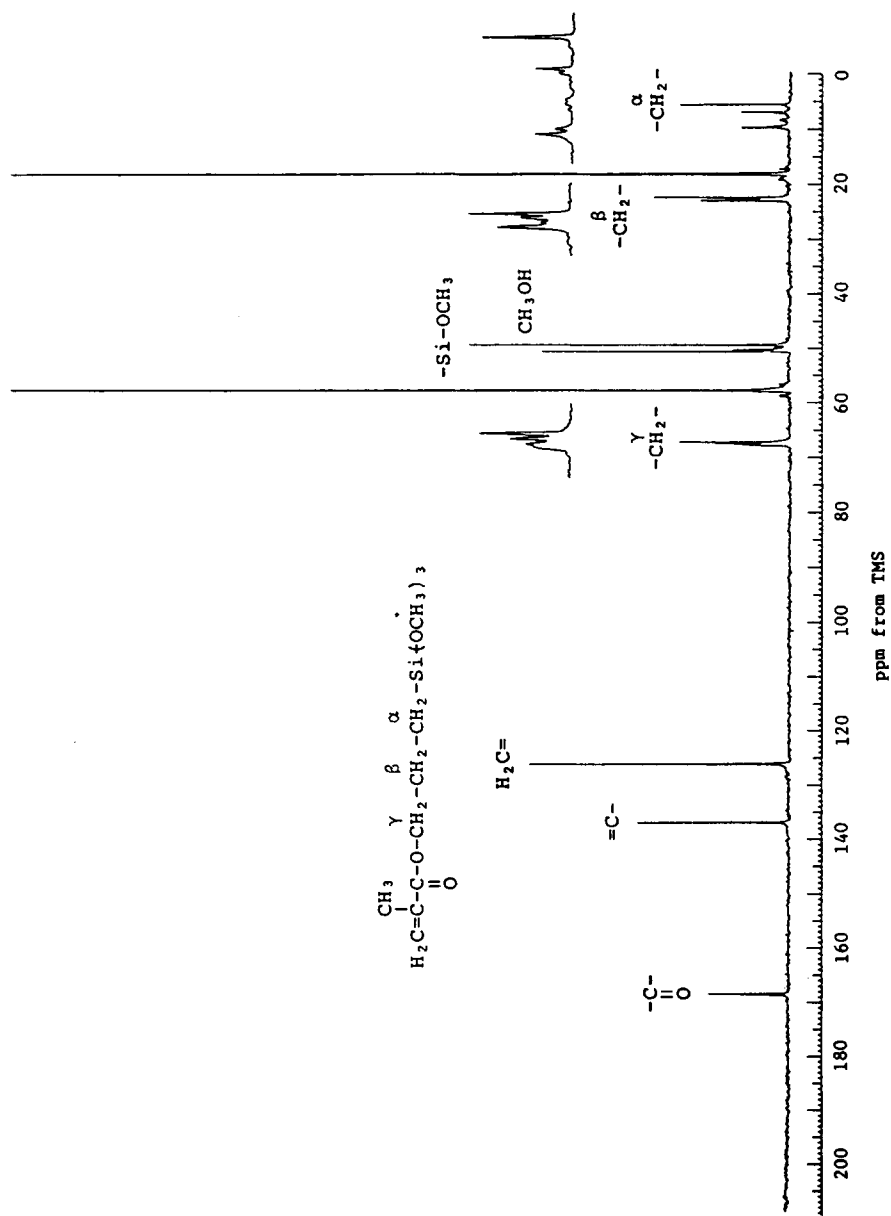


Fig. 1. ^{13}C NMR spectrum of γ -MPTS in $\text{EtOH}-\text{H}_2\text{O}$ (70 : 30 vol%) solvent system. Hydrolysis time: 2 days.

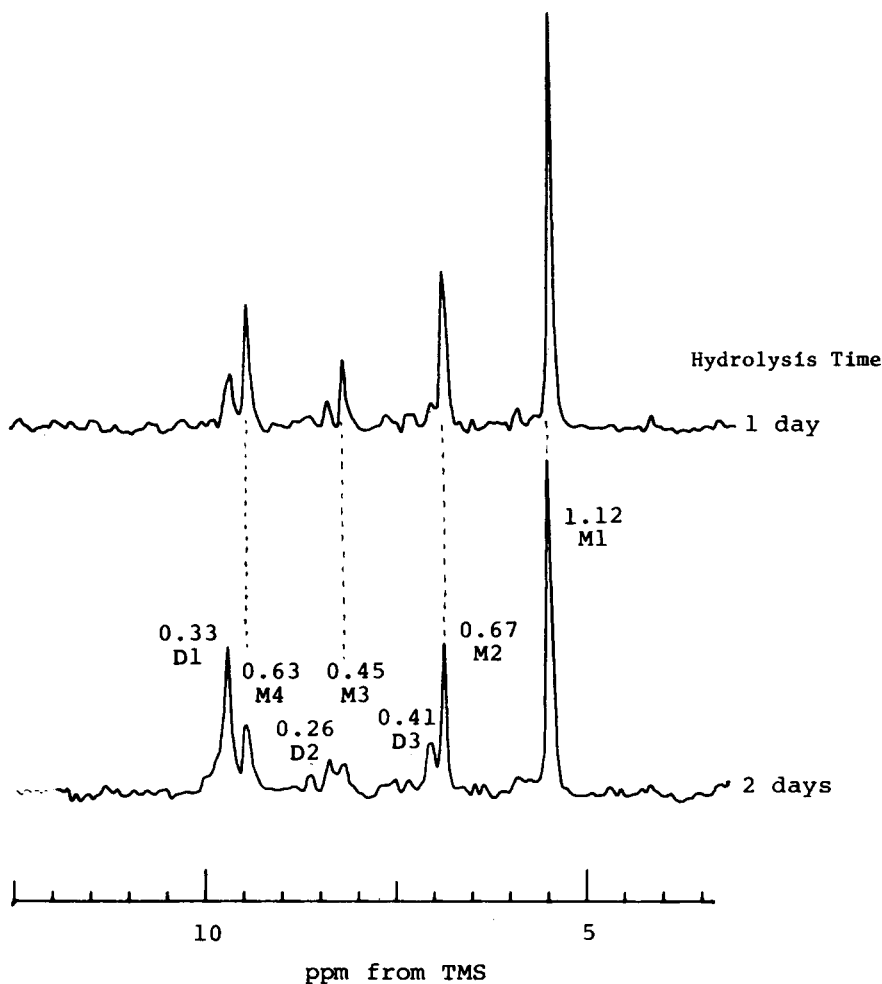


Fig. 2. The ^{13}C NMR spectra of the $\alpha\text{-CH}_2$ region of $\gamma\text{-MPTS}$ in $\text{EtOH-H}_2\text{O}$ (70:30 vol%) solvent system. The T_1 values (s.) were included.

carbons. As mentioned below, proceeding the condensation process, the $\alpha\text{-CH}_2$ peaks are concentrated at the D1 peak position and then, peak broadening occurs.

Assignment of the ^{29}Si NMR Peak of $\gamma\text{-MPTS}$

The ^{29}Si spectra of $\gamma\text{-MPTS}$ in 70 vol% $\text{EtOH-H}_2\text{O}$ solution are shown in Figure 3 periodically, together with the corresponding $\alpha\text{-CH}_2$ spectra. In the ^{29}Si spectrum of the first day, the sharp peaks are assigned M1–M4 to the lower fields because the relative intensities are in agreement with those of corresponding M1–M4 peaks in the ^{13}C NMR spectrum. In the course of time, condensation of hydrolysis species occurs, and the intensity of the ^{29}Si peaks of monomer species decreases. The peaks attributable to the dimerized species are observed at about -50 ppm, and assigned to D1, D2, and D3 peaks by referring to the relative intensities of the ^{13}C NMR peaks. Thus, the assignment to each Si atom was performed on the basis of a comparison of the ^{29}Si

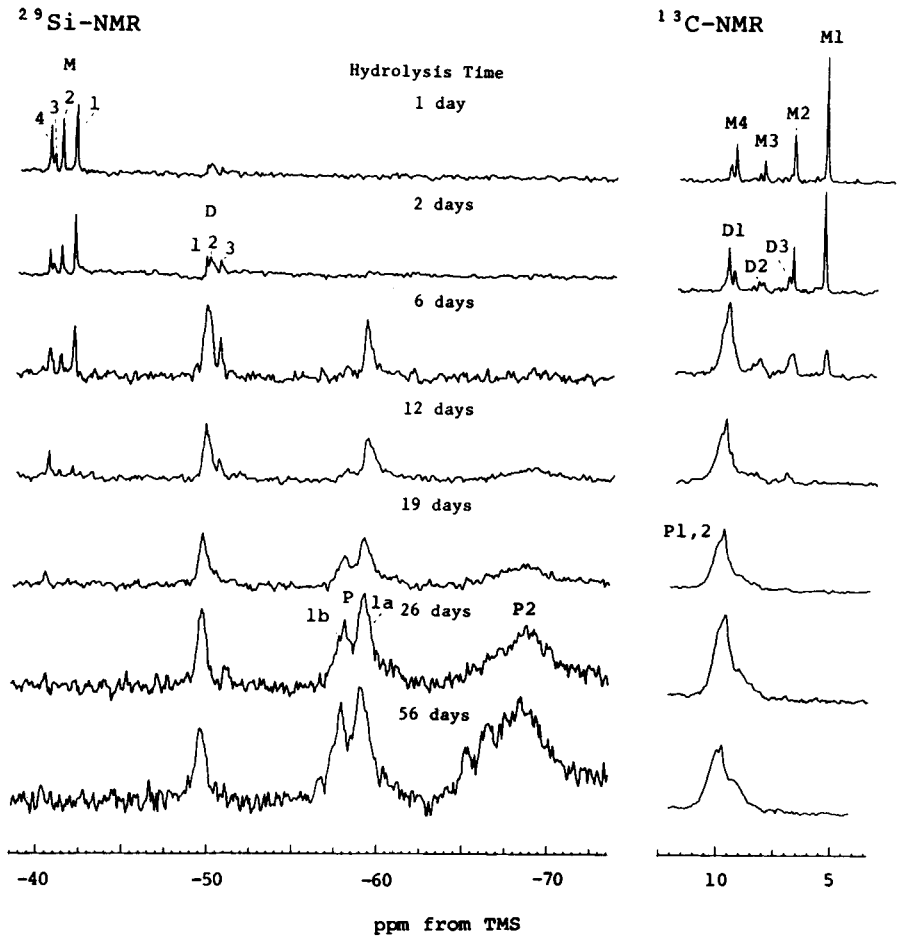
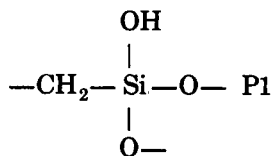


Fig. 3. ^{29}Si and ^{13}C NMR ($\alpha\text{-CH}_2$) spectra of $\gamma\text{-MPTS}$ in $\text{EtOH-H}_2\text{O}$ (70:30 vol%) solvent system as a function of the hydrolysis time.

and ^{13}C NMR spectra of $\gamma\text{-MPTS}$, at least, in the initial stage. Proceeding the condensation, the peaks attributable to



are observed at about -58 ppm and then, a broad peak resonating at -68.3 ppm is observed and assigned to

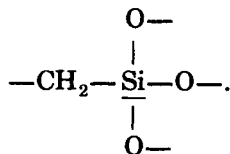


TABLE I
Assignment of ^{13}C ($\alpha\text{-CH}_2$) and ^{29}Si NMR Spectra of $\gamma\text{-MPTS}$

	Assignment	C δ (ppm)	T_1 (sec.)	Si δ (ppm)	T_1 (sec.)
M1	$\begin{array}{c} \text{OCH}_3 \\ \\ \text{CH}_2-\text{Si}-\text{OCH}_3 \\ \\ \text{OCH}_3 \end{array}$	5.6	1.12	41.8	41.8
2	$\begin{array}{c} \text{OCH}_3 \\ \\ \text{CH}_2-\text{Si}-\text{OH} \\ \\ \text{OCH}_3 \end{array}$	6.9	0.67	40.9	39.2
3	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2-\text{Si}-\text{OH} \\ \\ \text{OCH}_3 \end{array}$	8.3	0.45	40.5	24.3
4	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2-\text{Si}-\text{OH} \\ \\ \text{OH} \end{array}$	9.5	0.63	40.3	12.7
D1	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2-\text{Si}-\text{O}-\text{Si}-\text{CH}_2 \\ \\ \text{OH} \end{array}$	9.7	0.33	49.4	5.2
2	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2-\text{Si}-\text{O}-\text{Si}-\text{CH}_2 \\ \\ \text{OCH}_3 \end{array}$	8.5	0.26	49.7	
3	$\begin{array}{c} \text{OCH}_3 \\ \\ \text{CH}_2-\text{Si}-\text{O}-\text{Si}-\text{CH}_2 \\ \\ \text{OCH}_3 \end{array}$	7.2	0.41	50.2	
P1	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2-\text{Si}-\text{O}-\text{Si}-\text{CH}_2 \\ \\ \text{O} \\ \\ \text{CH}_2-\text{Si} \end{array}$			57.7 ^b 58.8 ^a	5.1 5.2
		9.9			
2	$\begin{array}{c} \text{CH}_2 \\ \\ -\text{Si}- \\ \\ \text{O} \\ \\ \text{CH}_2-\text{Si}-\text{O}-\text{Si}-\text{CH}_2 \\ \\ \text{O} \\ \\ -\text{Si}- \\ \\ \text{CH}_2 \end{array}$	10.0		68.3	4.2

The ^{29}Si NMR T_1 values are observed here, and the ^{29}Si CP/MAS chemical shift data of several kinds of Si compounds by Sindorf et al.^{5,6} supported these assignments. The Si NMR assignment is summarized in Table I, including the assignment of ^{13}C NMR spectra of the $\alpha\text{-CH}_2$ carbon atom, which bonded to the Si atom directly. The T_1 values are also listed.

The Mechanisms of Hydrolysis and Condensation of $\gamma\text{-MPTS}$

Depending on time, the relative area of the individual ^{13}C and ^{29}Si peaks of $\gamma\text{-MPTS}$ are shown in Figure 4. At the initial hydrolysis stage, the changes in the ^{13}C and ^{29}Si NMR relative intensities are within approximately 5% error. The relative intensity of starting material, M1, decreased rapidly and inversely, the intensities of the hydrolyzed monomer species, M2 to M4 increased after one day. However, the amount of these hydrolyzed monomer

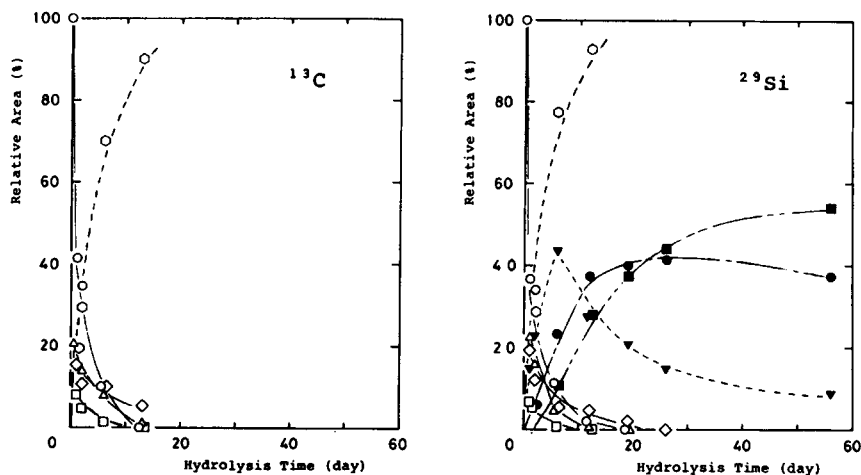
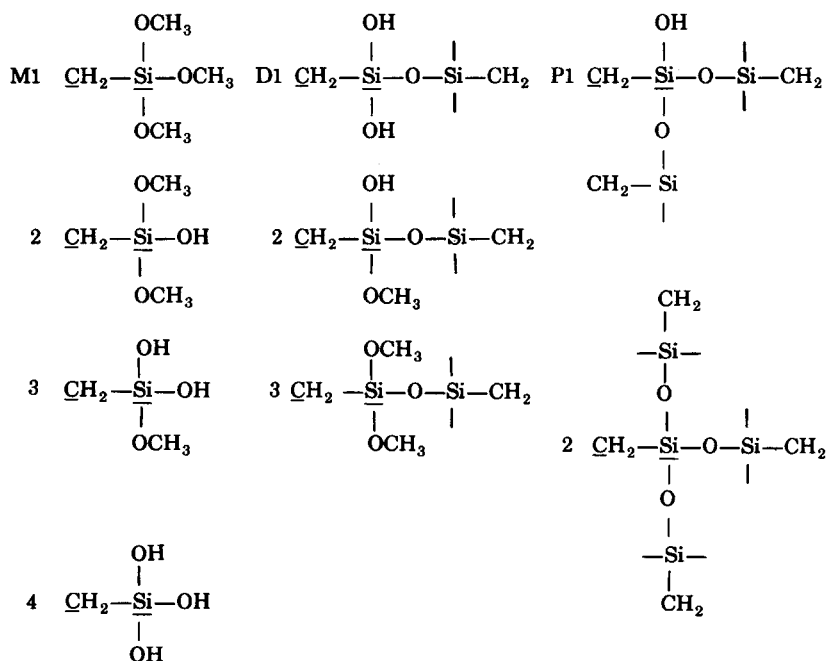


Fig. 4. The relative intensities of the α -CH₂ carbons and the ²⁹Si nuclei of γ -MPTS in EtOH-H₂O (70-30 vol%) solvent system as a function of the hydrolysis time: (○) M1; (Δ) 2; (□) 3; (◇) 4; (▼) D1, 2, 3; (●) P1; (■) 2; (○) D, P.



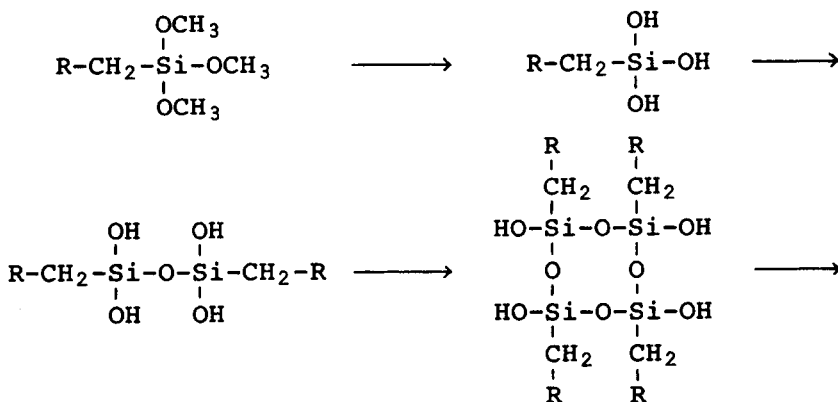


Fig. 5. High Molecular Weight Products. The hydrolysis and condensation mechanism of γ -MPTS in EtOH-H₂O (70:30 vol%) solvent system.

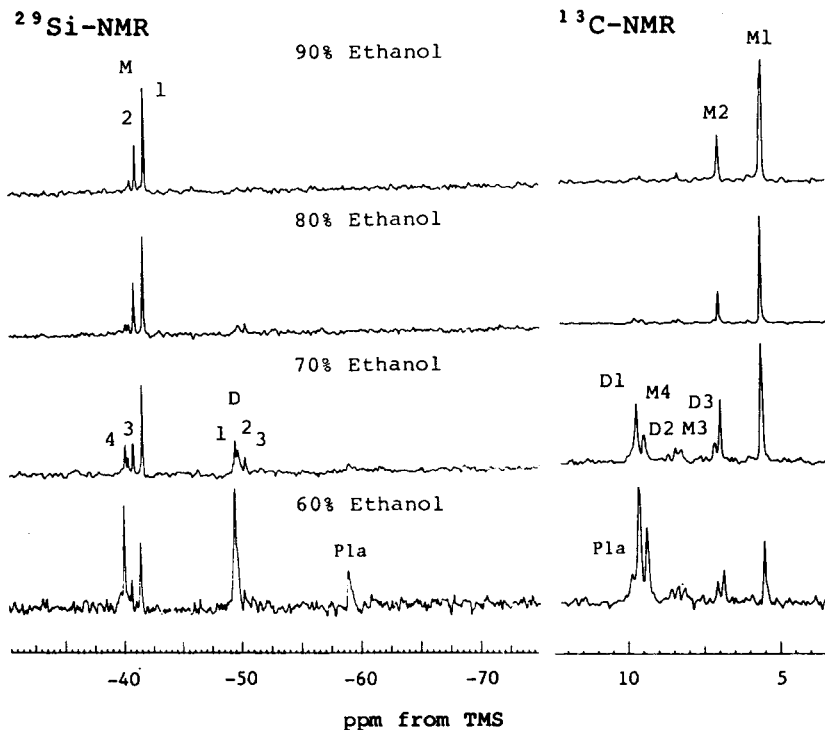
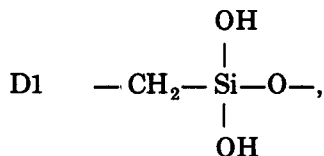


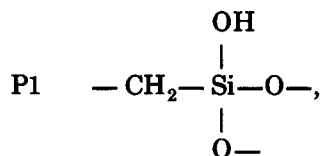
Fig. 6. The ²⁹Si and ¹³C NMR (α -CH₂) spectra of γ -MPTS as a function of water content in EtOH-H₂O solvent system. Hydrolysis time: 2 days.

decreased inversely after two days and that of the condensed dimer species,

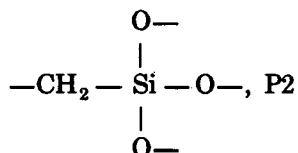


increased.

After 6 days, the condensed polymer species,



increased with a decreasing of the dimer species, D1. Finally, the peak attributable to



increased with a decreased P1 peak. Thus, the main mechanisms of hydrolysis and condensation of γ -MPTS is summarized in Figure 5. However, since there was not enough evidence to determine the structures of higher molecular weight products, the structures of these could not be analyzed from the NMR data. Miller et al.⁴ assigned the structure of the final products, condensed at above pH 4, to the double chain ladder configuration. It is thought that the structure of higher molecular weight products may be a double chain ladder configuration, assuming that their results are correct, since water pH is 5.7. As for the ^{13}C NMR spectrum, since the differences of the ^{13}C NMR chemical shifts of $\alpha\text{-CH}_2$ were very small among the condensed species, obtaining information about their condensation was impossible (Fig. 4). Ishida et al.¹³ determined the hydrolyzed species of γ -aminopropyltriethoxysilane in silane solution, using laser Raman method. The relative amounts of $-\text{Si}-(\text{OC}_2\text{H}_5)_3$ and $-\text{Si}-(\text{OH})_3$ was determined from the intensities of the $\text{Si}-\text{O}-\text{C}$ and $\text{Si}-\text{OH}$ bands only. However, as shown in Figure 4, there are several kinds of hydrolyzed and condensed species, contrary to the Ishida's analysis.

The ^{29}Si and ^{13}C NMR ($\alpha\text{-CH}_2$) spectra of γ -MPTS, which were hydrolyzed for 2 days, are shown in Figure 6 as a function of water content in EtOH-H₂O solution. The change in the relative area of the ^{13}C and ^{29}Si peaks coincide with each other as shown in Figure 7. The intensity of M1 peak decreased rapidly and inversely, that of M4 peak increased with increased water content. This means that water accelerates the hydrolysis.

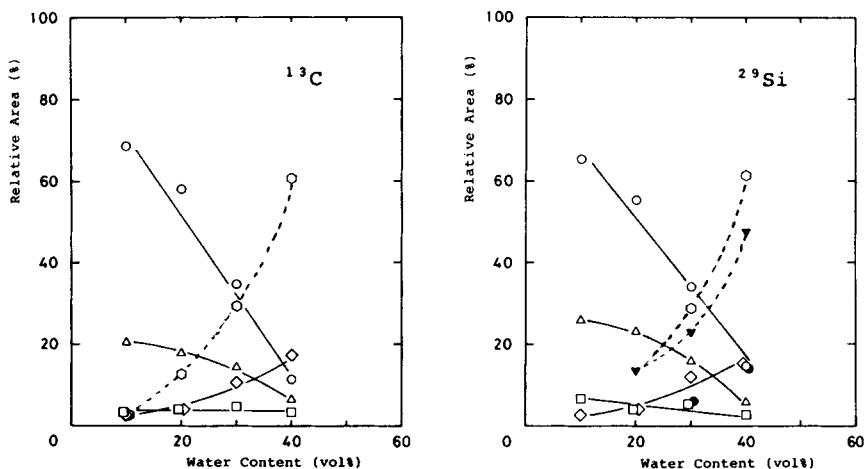
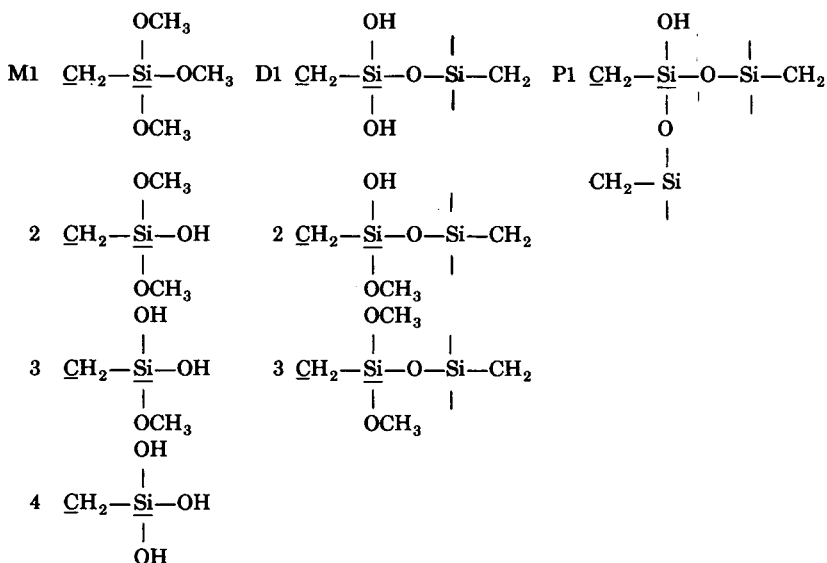


Fig. 7. The relative intensities of the α -CH₂ carbons and the ²⁹Si nuclei of γ -MPTS as a function of water content in EtOH-H₂O solvent system. Hydrolysis time: 2 days. (O) M1; (Δ) 2; (\square) 3; (\diamond) 4; (\blacktriangledown) D1, 2, 3; (\bullet) P1; (\circ) D, P.



CONCLUSION

The mechanisms of hydrolysis and condensation of a silane coupling agent were investigated by both ¹³C and ²⁹Si NMR spectroscopies. The species of the hydrolyzed monomer and the condensed polymer were assigned readily. The hydrolysis and condensation mechanisms of γ -MPTS are clear. Therefore, ¹³C NMR is suitable for analysis of hydrolyzed species in the initial step and ²⁹Si NMR is well suited for that of condensed species in the final step.

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